

## Rheokinetic model to characterize the maturation process of gelatin solutions under shear flow

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### ABSTRACT

The characterization of maturing gelatin solutions in shear flow is required for an appropriate formulation of food products. Under static conditions, the maturation process of gelatin solutions may be described through a basic structural parameter evolving to the percolation value (gel point). Within the rheological framework, two asymptotic viscosities are well identified for the maturing process of gelatin solutions at the limit zero shear rate. One involves the initial solution viscosity that may be associated with the null structural parameter (the microstructure is not formed yet). The other is the percolation zero shear rate viscosity (assuming an infinite value when approaching the gel time) and corresponds to the maximum value of the structural parameter. Under flow, thixotropic theories combined with the knowledge of suspension rheology allow one to convert directly experimental data obtained as shear stress versus time for a given shear rate into the time evolution of the structural parameter. Consequently rheometric experimental data available places the search for a rheokinetic model of the structural parameter. Here, different expressions for this model are investigated, mainly those involving both the rates of structure breakdown and buildup, where the average cluster size is affected by the shear rate. The rate equation thus obtained may be then applied to arbitrary shear rate histories. Numerical results of the rheokinetic model proposed in this work fit well experimental rheometric data obtained in shear flow for the maturing of different gelatin solutions. Experimental data acquired in this work are presented and discussed in relation to those reported previously in the literature.

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### 1. Introduction

The choice of gelatins for food products should be carried out by considering other properties apart from bloom strength and market price, having into account that these two factors are largely tied (Jones, 1977). Thus in addition to comparing gel strength and standard viscosity values among gelatin types, it is also recommended to evaluate gelatin solutions through different rheological tests. One of the most used procedures for this purpose is the classical rheometry evaluating linear viscoelastic properties, like the storage and dissipation moduli, measured at different frequencies of shear oscillations, either below or above the gel state. Although this test has proved to be useful in measuring the elastic properties of gels, conclusions obtained from these results are not enough to characterize fully the performance of gelatin solutions constituting food formulations. In fact, handling and processing of the precursor gelatin solution in the food industry require in

addition the knowledge of both the evolution of non-linear rheological properties and the practical estimation of the structural state of protein chains at the time of composing the food product. In this sense one should observe that the size and organization of protein clusters have an effect on the final texture of the resulting food network. Other operations involving coating and film formation, where the value of the shear rate may be significant, also require the rheological characterization of maturing gelatin solutions in the non-linear flow response. Another example may be found when a gelatin solution participates in a food emulsion as the continuous phase, where its thixotropic properties are of interest apart from the specific emulsifying function. Further, it has been shown that the combination of shear and elongational flows is relevant in the flow processing and gel formation for the shape design of gelatin drops to create special structure in food products (Walther, Walkenström, Hermansson, Fischer, & Windhab, 2002).

Within this brief context of analysis of gelatin applications in the food industry, it is clear that additional rheometric tests characterizing gelatin solutions in non-linear flows may be useful, mainly when the role of different values of classical properties like bloom, standard viscosity, isoelectric point, protein amino acid sequence, concentration, etc., affects the solution thixotropic response, which is a consequence of the formation of a rather complex network

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structure. Here one should observe that in the conventional dynamic rheometry of maturing gelatin solutions, mainly the structure buildup process generated during maturation is measured, because in general the dissipation modulus is quite difficult to be sensed at the rather small deformations required by a meaningful linear viscoelastic test (Braidot & Deiber, 1999). Although the breakdown process is important indicating the resistance of the network being formed in the maturation process, which is in part intrinsic to each type of gelatin used, linear viscoelastic properties cannot provide the magnitude of this process. In the present work, by considering the shear response of maturing gelatin solutions, we will show that there exists a critical gelatin concentration for which the breakdown process may exceed the build up process and the expected structure due to which gelling remains unformed. Thus the parameter values that characterize a gelatin solution are directly related to its non-linear rheological response, which in turn allows one to visualize the global performance of the type of gelatin selection in a wide range of possibilities.

More specifically, the maturation process of gelatin solutions through physical crosslinks involves significant microstructural changes. Thus, dissolved random polypeptide chains are reverted to partial tropocollagenic triple helices generating either disordered networks under static conditions or suspensions of chain clusters under shear flow (De Carvalho & Djabourov, 1997; Huang & Sorensen, 1996). Under static conditions, this process starts from the initial solution and evolves toward the gel state (the percolation point), where the apparent viscosity function at near zero shear rate increases to very high values before fracture. Between these two basic states, the macroscopic evolution of gelatin solutions may be sensed as a thixotropic fluid response through the apparent viscosity function evaluated in shear flow, in which the microstructure is destroyed mechanically (breakdown process) and simultaneously formed kinetically (build up process) at relatively higher rates than those of conventional thixotropic materials formed by concentrate pastes and particle suspensions. In this sense, it is appropriate to observe that all shear-thinning materials are in principle thixotropic, because a finite time is required to produce microstructural reorders necessary to respond mechanically as shear-thinning (Barnes, 1997, 1999). Therefore, under flow, it is expected after a given time the formation of an equilibrium structure that depends on the value of an appropriate measure of the rate of deformation process. This measure is typically the shear rate in most studies carried out and reported in the literature (Barnes, 1997, 1999; Bauer & Collins, 1967; Cheng, 1987; Dullaert & Mewis, 2005, 2006; Mujumdar, Beris, & Metzner, 2002) and alternatively invariants of the rate of deformation tensor (Mewis, 1979). It is then clear that the predictive expectations from a tensorial constitutive model of thixotropic materials may meet several limitations due to the complexity found within the actual comprehension of this subject. A discussion on this aspect is presented by Beris, Stiakakis, and Vlassopoulos (2008). This situation places practical applications, and partly the research framework, into studying mainly simple 1-D mechanical histories like, for instance, sequences of shear rates (steps up and down), shear rate loops (also designated thixotropic loops) and other tests expressed through specific designed time functions of the shear rate, which may help to visualize microscale mechanisms associated with the breakdown and build up rate processes. Most of the constitutive equations for thixotropy that apply to arbitrary shear rate flows have been well presented and tabulated by Mujumdar et al. (2002), where they are classified into two groups: (a) phenomenological models and (b) structural kinetic models. This last one may be also secondarily classified as direct and indirect models. At present, the indirect structural kinetic model has gained more attention in the literature, perhaps due to its apparent simplicity. For example Mao

and Chen (2006) used this type of model to study the thixotropy of locus bean in sucrose solutions. The indirect structural kinetic model is also the main subject of the present work, where the maturation process of gelatin solutions is studied.

Although thixotropy may be found in a wide spectrum of material types, at present it is quite evident that for Brownian aggregating particle suspensions, common characteristics are responsible for the thixotropic response under deformation: the state of segregation and size of clusters forming the discrete phase in the suspending fluid change for each pair of values of shear rate and maturation time. In the particular case of gelatin solutions, the fluid state at a given maturation time may be found to depend on the previous mechanical history coupled to nucleation and growth of clusters in rather complex mechanisms (De Carvalho & Djabourov, 1997), which depend on the type of gelatin as well as on some physicochemical conditions, like for instance, protein concentration (see Section 4.1 below).

From the above phenomenological description, it is interesting to indicate here that the rheokinetics of maturing gelatin solutions (aqueous solvent with dissolved macromolecules reverting partially to the tropocollagenic structure) is prone to be studied in shear flow (De Carvalho & Djabourov, 1997; Huang & Sorensen, 1996) in order to get relevant information concerning the microstructure evolution of food products. We propose to study these solutions as thixotropic fluids, based mainly on the following aspects: (a) the rate of structure formation competes with the breakdown process in relatively small time intervals, placing thus emphasis in the thixotropic response more than in the asymptotic pseudoplastic behavior manifested for a very rapid structure reconstruction (Barnes, 1997) or very slow structure build up of conventional thixotropic suspensions; (b) the rheological response is detected following the inverse process of classical studies in thixotropy; thus, shear rheometric tests may be carried out from the fully unstructured fluid (initial solution) toward the progressively structuring material resulting from the maturation process; (c) in this context of analysis a structural parameter may be introduced, which is evaluated directly from measurements of the apparent viscosity function. Baravian, Quemada, and Parker (1996) applied this last concept to study the thixotropy of *iota* carrageenan solutions.

Within this framework, we present here a rheokinetic model susceptible to be evaluated computationally to characterize the maturing process of gelatin solutions in shear flow, based on the indirect structural kinetic model approach. Therefore, in Section 2 the experimental program involving different shear rate histories is described in details for solutions formulated with a gelatin obtained from bovine skin. Here other experimental data reported in the literature are also processed for further analysis and comparison in the discussion of results. Based on these data, a rheokinetic model is proposed in Section 3, where a numerical method is required to obtain solutions and validate asymptotic values of the structural parameter and the apparent viscosity function along maturation time. Finally, in Section 4 numerical and experimental results are analyzed in relation to model characterization and predictions and to microstructure considerations. The most relevant conclusions are presented in Section 5.

## 2. Experimental program

### 2.1. Materials and methods

Experimental rheokinetic tests were carried out with a gelatin sample provided by PB Leiner Gelatin Argentina (isoelectric point pI 4.8, and standard viscosity at 60 °C and 6.66% w/w of 3.9 mPa s; the gelatin was obtained from bovine skin, with  $M_n \approx 133$  kDa). Aqueous solutions were prepared by hydration of the commercial gelatin powder with deionized water at 50 °C for around 15 min.

Then the hydrated slurry was completed with the water required to get a particle suspension with a protein concentration of 6.66% w/w, which was subjected to magnetic stirring by still keeping a constant temperature of 50 °C until a dissolution was achieved (around 45 min were needed). Also, 0.02% of sodium azide was added to prevent bacterial degradations during the maturation period and experimental tests. This type of solution is designated Sample I throughout this work. Solutions are prepared at the beginning of each rheometric test to avoid secondary effects in the maturation process. They are also filtered and subjected to maturation at a fixed temperature for each experiment. Shear rate rheometric tests are carried out in a cone–plate cell with a cone angle  $\alpha_0 = 1.565^\circ$ . Following classical symmetry considerations, one finds that the stress tensor in shear flow may be described through three rheometric functions. Here we have special interest on experimental data of the apparent viscosity function  $\eta(\dot{\gamma})$ , which is more susceptible to be analyzed within the thixotropic theoretical background. From the above considerations, it is well known that in a cone–plate rheometric cell one obtains a uniform shear rate in the whole flow domain, expressed as  $\dot{\gamma}(t) = \Omega(t)/\alpha_0$ , where  $\Omega(t)$  is the controlled cone angular velocity. Consequently, the appropriate evaluation of the torque  $M(t)$  that the fluid exerts on the cone leads one to obtain the required apparent viscosity function through  $\eta(\dot{\gamma}(t)) = 3M(t)\alpha_0/2\pi R_0^3\Omega(t)$ , where  $R_0$  is the plate radius. These expressions apply to programmed changes of the angular velocity  $\Omega(t)$ ; thus different shear rate histories may be considered to evaluate numerically the rheokinetic structural model proposed and discussed below. In this context of analysis, the maturation of gelatin solutions is carried out for the following mechanical histories: (A) Sudden inception of constant shear rates according to  $\dot{\gamma}(t) = \dot{\gamma}_i H(t)$ , where  $H(t)$  is the Heaviside step function and  $\dot{\gamma}_i$  is a defined value of shear rate. Curves of  $\eta(t)$  as a function of maturation time  $t$ , at different  $\dot{\gamma}_i$  are thus obtained. (B) Increasing and decreasing consecutive steps of suddenly imposed shear rates  $\dot{\gamma}_i$  at different times  $t_i$ . Thus, one has  $\dot{\gamma}(t) = \sum_{i=1}^3 \dot{\gamma}_i H(t - t_i)$ . (C) Thixotropic loops, where the shear rate is increased linearly from an initial minimum  $\dot{\gamma}_{\min}$  to a maximum  $\dot{\gamma}_{\max}$  obtained at time  $t_{\max}$ ; then the shear rate is decreased, also linearly, to obtain again the value  $\dot{\gamma}_{\min}$  at a total test time of  $2t_{\max}$ . Although these rheometric tests are well defined from the theoretical point of view within the framework of the above equations, in practice the control of  $\Omega(t)$  may introduce undesired inertial effects. Thus, these effects require a correction, which is not a trivial procedure (Baravian et al., 1996) or alternatively measurements shall be carried out at times different from those where the shear rate is suddenly changed, as indicated below. In this sense, inertial effects associated with the cone of the rheometric cell satisfies the angular momentum balance, which for test B yields,  $M = M_e - J\alpha_0 \sum_{i=1}^3 \dot{\gamma}_i \delta(t - t_i)$ , where  $J$  is the cone inertial moment,  $M_e$  is the restoring moment of the cone bar and  $\delta(t)$  is the Dirac delta-function. Thus at times  $t_i$  the second term in the right hand side of this equation takes sharp values masking the expected measurement based strictly on  $M \approx M_e$ . Therefore, here torque values are taken for  $t \gg t_i$ , around 60 s after each value of  $t_i$  in tests A and B. In test C another experimental problem must be considered. In fact,  $\Omega(t)$  is not varied smoothly in most commercial rheometers. This process is carried out, however, through small steps of both time and shear rate, of the order of 10 s and  $4 \text{ s}^{-1}$ , respectively, for the viscometer used in this work. Thus inertial effects are more important for test C than for tests A and B, described above. To minimize them, measurements are taken at times just before the small steps of shear rates are introduced after each time intervals of around 10 s. In general, it is required to increase either the total time or to decrease the maximum shear rate of the loop to minimize inertial effects. Therefore, based on tests A, B and C, the following experimental protocols were carried out: E-1: Gelatin solutions required to

measure the apparent viscosity were matured for a period of time of around 30 min at different maturation temperatures (24, 25, 26 and 27 °C each one for 3.8, 7.6, 14.4, 26.6, 49.4, 76, 106, 152, 190, 209, 228, 266 and  $418 \text{ s}^{-1}$ ). This study showed us that the optimum temperature to get a wide shear rate sweep was 26 °C. E-2: Gelatin solutions were matured during 30 min at 26 °C at a constant shear rate. In this period measurements of the apparent viscosity are carried out each 60 s upon the sudden inception of each 13 different constant shear rates. This experiment is useful to determine functions and parameters of the rheokinetic model, and to establish the range of shear rate where measurements are stable. E-3: Gelatin solutions were matured during 30 min at 26 °C. In this period, measurements of the apparent viscosity are carried out each 60 s for two different sequences of three increasing and decreasing steps of shear rates, viz., 106–209–419  $\text{s}^{-1}$  and 418–209–106  $\text{s}^{-1}$ . This experiment is useful to study the discontinuity of shear rate histories in the rheokinetic model. E-4: Gelatin solutions were matured during 30 min at 26 °C, and measurements of the apparent viscosity are carried out each 10 s for a symmetric thixotropic loop starting at 76  $\text{s}^{-1}$ , reaching a maximum of 247  $\text{s}^{-1}$  and finally decreasing to 76  $\text{s}^{-1}$  again. For shear rates below 50  $\text{s}^{-1}$ , flow instabilities are observed (see also Section 4.1) in coincidence with data reported by De Carvalho and Djabourov (1997).

Another gelatin sample provided by SIGMA for R&D purposes (isoelectric point pl 5; the gelatin was obtained from bovine skin, with  $M_n \approx 45 \text{ kDa}$ ) was also studied in this work to evaluate the effect of gelatin concentrations on the rheokinetic evolution of gelatin solutions under shear flow. This type of solution is designated Sample II throughout this work.

For all rheometric experiments a Digital Brookfield Rheometer (DV-III model) controlled through a PC was used. This system includes the Rheocalc program for data processing. The closed cone–plate cell was connected to a thermostatic bath that controls the temperature with a precision of  $\pm 0.01$  °C.

## 2.2. Experimental data available in the literature

To visualize the performance of the rheokinetic model proposed here at high values of maturation times, we also used experimental data of the apparent viscosity function concerning the maturation of gelatin solutions at different constant shear rates (test A described above) for maturation times as long as 1000 min, reported by De Carvalho and Djabourov (1997). The gelatin solutions were 6.5% w/w in protein and tests were carried out at 26 °C. This type of solution is designated Sample III throughout this work. This photographic grade gelatin was obtained from bones, with  $M_n \approx 215 \text{ kDa}$ . For more dilute gelatin solutions of around 3% w/w, Huang and Sorensen (1996) also reported the apparent viscosity function of maturing gelatin solutions at 28 °C for different constant shear rates (test A described above) and for maturation times as long as 2650 min. This type of solution is designated Sample IV throughout this work. The gelatin used was also obtained from bone with  $M_w \approx 120 \text{ kDa}$ . For this purpose experimental data are generated from the original curves reported by these authors. To our best knowledge, these are the only experimental data available in the literature concerning the shear flow of maturing gelatin solutions, useful to be analyzed through structural kinetic models.

## 3. Modeling the maturation process of gelatin solutions

### 3.1. Constitutive model for the apparent viscosity function

Throughout this work the maturing process of gelatin solutions may be described by a generic structural parameter  $\Gamma$  that evolves to the percolation value  $\Gamma_c$  under static conditions (no flow is imposed) and hence, it is convenient to define the normalized

structural parameter  $\lambda = T/T_c$  for the indirect structural kinetic model describing the basic gelling process. Since the phenomenological description is carried out for rheometric responses comprised between the primitive solution and the suspension approaching to the gel point, only the fluidic character of this material is considered here. Within this modeling framework of thixotropic gelling solutions, the relationship between shear stress  $\tau(t)$ , shear rate  $\dot{\gamma}(t)$  and the normalized structural parameter  $\lambda(t, \dot{\gamma}(t))$  has been formulated through different expressions in the literature, which are not necessarily equivalent. Thus, one may start by considering that the apparent viscosity function  $\eta = \tau/\dot{\gamma}$ , defined at a given temperature, is a function of the structural parameter through the expression  $\eta(t) = \eta(\lambda(t, \dot{\gamma}), p_i)$ , where  $p_i$  is a physical constant. Within this framework, one finds the relation proposed by Baravian et al. (1996) indicating that the normalized structural parameter is related to the apparent viscosity function through the following expression,  $\eta = \eta_\infty / (1 - K\lambda)^2$ , where  $K = (1 - \sqrt{\eta_\infty/\eta_0})$ . Here,  $\eta_\infty$  and  $\eta_0$  are the limiting Newtonian viscosities at zero and high shear rates. Therefore, for maturing gelatin solutions we considered here that at a shear rate asymptotically null ( $\dot{\gamma} \rightarrow 0$ ) the condition  $\lambda = 1$  is achieved at the percolation point and hence  $\eta_0 \rightarrow \infty$ . Also, at the initial time, the solution viscosity  $\eta_s$  corresponds to the equilibrium viscosity value  $\eta_\infty$  when  $\lambda = 0$  (the aggregates of the microstructure are not present or are fully broken). Thus, one obtains  $K = 1$  and the resulting apparent viscosity function in this specific problem including the percolation point is,

$$\eta(\lambda(t, \dot{\gamma}), \eta_s) = \eta_s / (1 - \lambda(\dot{\gamma}, t))^2 \quad (1)$$

Therefore, it is clear that from the rheological point of view (thus as long as flow is under analysis only) one recognizes two asymptotic responses of the maturation process of gelatin solutions. These definitions allow one to convert directly experimental data obtained as shear stress  $\tau(t)$  versus maturation time  $t$  for a given rate of deformation history  $\dot{\gamma}(t)$  into the evolution of the normalized structural parameter  $\lambda(t, \dot{\gamma}(t))$ . Consequently, this evolution places the search for a kinetic expression  $\dot{\lambda} = g(t, \dot{\gamma}(t))$ . The rate equation thus obtained may then be applied in principle to arbitrary rate of deformation histories. Here we investigate computationally different expressions for  $g(t, \dot{\gamma}(t))$ , mainly those involving both the rates of structure breakdown and buildup, where the sizes of clusters are governed by the value of the shear rate at a given maturation time (De Carvalho & Djabourov, 1997).

### 3.2. Kinetic equation for the structural parameter

The determination of function  $g(t, \dot{\gamma}(t))$  through basic rheometric data is not a simple task. From the analysis of the literature and taking several basic studies for different thixotropic systems (Møller, Mewis, & Bonn, 2006) we propose here a quite general equation described as follows,

$$\dot{\lambda} = k(1 - \lambda)^{q(\dot{\gamma})} \lambda^c - X(\dot{\gamma})\lambda \quad (2)$$

where  $X(\dot{\gamma})$  is the breakdown function satisfying  $X(0) \rightarrow 0$ . Also,  $k$  is a kinetic constant, and  $q(\dot{\gamma}) > 0$  (constrained to  $q(0) \geq 1$ ; see also below) is associated with the kinetic order of the build up process, proportional to the distance from the actual structural state  $\lambda$  to the percolation state  $\lambda = 1$ , where one expects to find an infinitely high asymptotic apparent viscosity. In Eq. (2),  $c$  is a constant close to one, although in some gelling material  $c = 0$  is required because the initial increase of the normalized structural parameter is quite rapid. Also it is assumed that the breakdown process is proportional to the amount of structure formed at present time  $t$ . One considers here that in shear flow,  $\lambda$  evolves through two basic mechanisms, one involves the growing of microstructure, which is mainly concerned

with attractive forces and the participation of the associated Brownian movement, and the other considers the breakdown of microstructure by mechanical forces (here in particular that caused by shear rate). Most of the structural kinetic equations proposed in the literature may be derived from Eq. (2) mainly by selecting appropriate expressions for  $X(\dot{\gamma})$  and  $q(\dot{\gamma})$ . For the particular case  $\dot{\gamma} \rightarrow 0$ ,  $c = 0$  and  $q(0) = 1$ , the normalized structural parameter satisfies,

$$\lambda(t, 0) = 1 - \exp(-kt) \quad (3)$$

which is able to describe an asymptotic sol–gel transition as the maturation time increases (see also Eq. (2)). Also, for the particular case  $q(0) > 1$  and  $\dot{\gamma} \rightarrow 0$ , one readily finds,

$$\lambda(t, 0) = 1 - \frac{1}{[1 + (q - 1)kt]^{1/(q-1)}} \quad (4)$$

which is able to describe a rather smooth asymptotic sol–gel transition as the maturation time increases. It is then clear from comparing Eqs. (3) and (4) that  $\dot{\gamma} \rightarrow 0$  and  $q(0) = 1$  are strict conditions to approach rather sharply the sol–gel transition. Further, one infers that for  $\dot{\gamma} \neq 0$  the two right hand terms of Eq. (2) survives, thus not allowing the material to reach the percolation point ( $\lambda \rightarrow 1$ ). This result is clearly validated by the experimental data analyzed in Section 4 below. For  $\dot{\gamma} \neq 0$ , one expects to find a suspending phase composed of growing clusters of the macromolecules dissolved in the solvent when the shear rate is constant. This phase may have an equilibrium state value  $\lambda_e$  of the structural parameter  $\lambda$  at high maturation times described by the condition  $g(\lambda_e, \dot{\gamma}) = 0$ . Consequently from Eq. (2) and in particular for  $q(\dot{\gamma}) = 1$ ,  $c = 0$  and a constant shear rate, it is readily found,

$$\lambda_e(\dot{\gamma}) = \frac{k}{k + X(\dot{\gamma})} \quad (5)$$

where,  $\lambda_e(\dot{\gamma})$  is clearly a decreasing function of shear rate (numerical solutions are required to obtain more generic expressions from Eq. (2)). Once more, from a different point of view, Eq. (5) demonstrates that the percolation point is achieved only for  $\dot{\gamma} \rightarrow 0$ . For instance one gets,

$$\lambda_e(\dot{\gamma}) = \frac{k}{k + k_1 \dot{\gamma}^p} \quad (6)$$

where  $X(\dot{\gamma}) = k_1 \dot{\gamma}^p$  is a classical assumption. Consequently, Eq. (6) shows that the percolation point ( $\lambda(t_g, 0) = \lambda_e \rightarrow 1$ ) is achieved for  $\dot{\gamma} \rightarrow 0$  only, where  $t_g$  is the time required to approach the gel point. Also, as a first approximation, the maturation kinetic order under shear may be  $q(\dot{\gamma}) \approx 2$  as a consequence of a pair macromolecular interaction, leading to the following physical equilibrium value from two mathematically possible solutions,

$$\lambda_e(\dot{\gamma}) = (1 + m) - [(2 + m)m]^{1/2} \quad (7)$$

where  $m = k_1 \dot{\gamma}^p / 2k$ . Interesting is the fact that once more  $\lambda_e \rightarrow 0$  for  $\dot{\gamma} \rightarrow \infty$  (see Eq. (6)). This result shows in a clear trend that when  $q(\dot{\gamma})$  is an increasing function of shear rate in Eq. (2), the true value  $\lambda_e$  shall be determined numerically because the functions assumed above to obtain analytic expressions (Eqs. (3)–(7)) are usually too simple for practical applications, although they are qualitatively correct. In fact, it is found below that  $q(\dot{\gamma}) \approx 2$  is a first approximation for the maturation of gelatin solutions under shear for the concentration range studied here.

An analytic solution of Eq. (2), for  $X(\dot{\gamma}) = k_1 \dot{\gamma}^p$ ,  $q(\dot{\gamma}) = 1$  and  $c = 0$ , may be readily obtained for a constant shear rate,

$$\lambda(t, \dot{\gamma}) = \frac{k}{(k + k_1 \dot{\gamma}^p)} \left\{ 1 - \exp \left[ - \left( k + k_1 \dot{\gamma}^p \right) t \right] \right\} \quad (8)$$



This equation shows simply that  $\lambda \rightarrow \lambda_e = k/(k + k_1 \dot{\gamma}^p)$  and  $\lambda = 0$  for  $t \rightarrow \infty$  and  $t \rightarrow 0$ , respectively, and  $\lambda_e \rightarrow 0$  for  $\dot{\gamma} \rightarrow \infty$ , as expected physically following the concepts mentioned above. One concludes here that the above asymptotic solutions of Eq. (2) are relevant to validate the numerical solution of the full structural kinetic equation, and also to elucidate the thixotropic behavior of gelling gelatin solutions, as described below.

### 3.3. Numerical solution of the model proposed

The model proposed here for the shear stress response of maturing gelatin solutions is composed of Eqs. (1) and (2). Conversely, experimental information concerning the structural parameter is obtained through inversion of Eq. (1) when data of the apparent viscosity function from the rheometric cell are available. Consequently the numerical prediction of  $\lambda$  through Eq. (2) must fit data of the structural parameter. The numerical code generated for this purpose has the following steps: (1) Expressions for  $X(\dot{\gamma})$  and  $q(\dot{\gamma})$  are selected by following the trend of preliminary results and studies (see also Section 4.1 below). (2) Then Eq. (2) is written in finite differences and the Runge–Kutta algorithm of fourth order is introduced to seek solutions  $\lambda(t, \dot{\gamma})$  for sudden inceptions of different constant shear rates (results from test A are used as basic data). (3) Numerical results obtained for  $\lambda$  are compared with experimental values reported at the same shear rate step through Eq. (1). This procedure allows one to evaluate and fix functions and constants of the rheokinetic model. The fitting process follows several simple rules. For instance,  $k$  is estimated from the slope of the curve  $\lambda$  as a function of time at  $t = 0$ , as indicated by Eq. (2) with  $\lambda(0) = 0$ . Further,  $k$ ,  $X(\dot{\gamma})$  and  $q(\dot{\gamma})$  control the asymptotic value  $\lambda_e$  observed in the experimental data, as predicted by analytical expressions (Eqs. (5) and (6)) for  $c = 0$  and  $q = 1$ . It is then clear that increasing the shear rate,  $q(\dot{\gamma})$  increases and  $\lambda_e$  decreases toward a lower equilibrium value with a smaller equilibrated cluster size on the average (see Section 4.2 below). (4) From steps (1) to (3) the structural kinetic equation (Eq. (2)) is fully determined (function  $g(t, \dot{\gamma}(t))$  is known now); hence the model is able to predict the apparent viscosity function for other shear rate histories  $\dot{\gamma}(t)$  (tests B and C) by using the same algorithms described above with the functions and parameters already evaluated in steps (1)–(3).

## 4. Results and discussion

### 4.1. Model characterization and predictions in relation to experimental tests

Following the considerations established in Section 3.3 concerning the numerical method, it is clear that test A allows one to determine the rheokinetic model's characteristic functions and constants designated as  $X(\dot{\gamma})$ ,  $q(\dot{\gamma})$ ,  $k$  and  $c$ , for a specific gelatin solution. Therefore, the challenge here is that once these functions and constants of a given gelatin solution have been fixed through test A, they must be the same when numerical predictions are compared with experimental data, for instance, from tests B and C, to get thus physical consistency of the formulation of Eq. (2). Results for Sample I are reported in the caption of Fig. 1a and b. In this figure it is illustrated the model fitting of the structural parameter and hence the apparent viscosity. We observe that  $X(\dot{\gamma})$ ,  $q(\dot{\gamma})$ ,  $k$  and  $c$  provided were able to fit the whole set of experimental data for a wide range of constant shear rates (from 76 to 418 s<sup>-1</sup>). Here, shear rates lower than 50 s<sup>-1</sup> were not considered and a discussion of this aspect is presented below in relation to our experimental results as well as those discussed by previous authors.

As a second step to validate the model, experimental data concerning test A of Sample III was used. The model fitting through

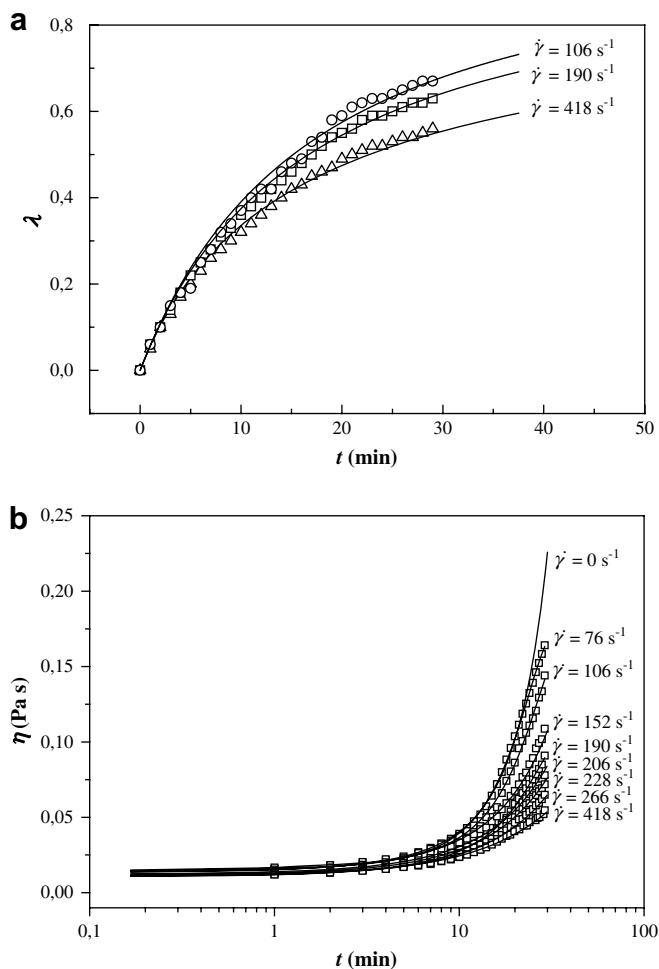
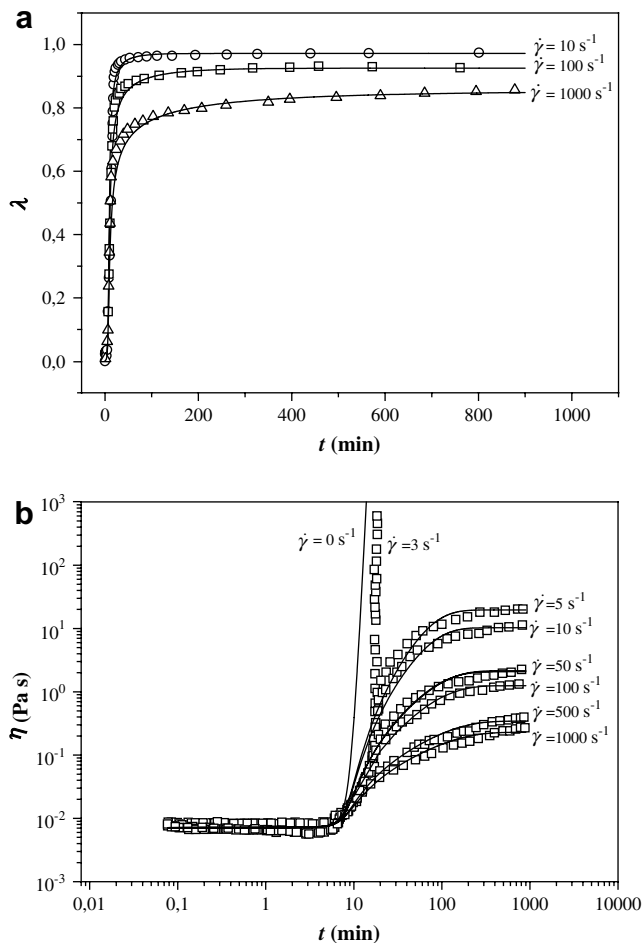


Fig. 1. (a) Normalized structural parameter  $\lambda$  and (b) apparent viscosity function  $\eta$  as a function of maturation time  $t$  for different shear rates following test A and protocol E-2. Symbols are experimental data of Sample I. Full lines are numerical predictions of the rheokinetic model, where parameters and functions are  $k = 10^{-3}$  s<sup>-1</sup>,  $c = 0$ ,  $X = 10^{-9} \dot{\gamma}^{1.3}$  and  $q = (1.788 + 0.015 \dot{\gamma})^{0.5}$ .

Eq. (2) of the experimental structural parameter data obtained from Eq. (1) is illustrated in Fig. 2a. Fig. 2b shows the numerical prediction of the corresponding apparent viscosity function. The characteristic functions and constants of the rheokinetic model are reported in the figure caption. Once more one observes an appropriate response of the model mainly for relatively high values of shear rates in a similar fashion as described for Fig. 1. In Fig. 2 the experimental information covers higher values of maturation times making more relevant the appropriate model response. Numerical predictions are depicted through the apparent viscosity function versus maturation time in Fig. 2b for the whole range of shear rate values, including also those lower than 50 s<sup>-1</sup>, where the theoretical prediction of the percolating curve is visualized for the asymptotic prediction of the percolating curve, which is close to experimental values corresponding to a low shear rate of 3 s<sup>-1</sup>, as one expects.

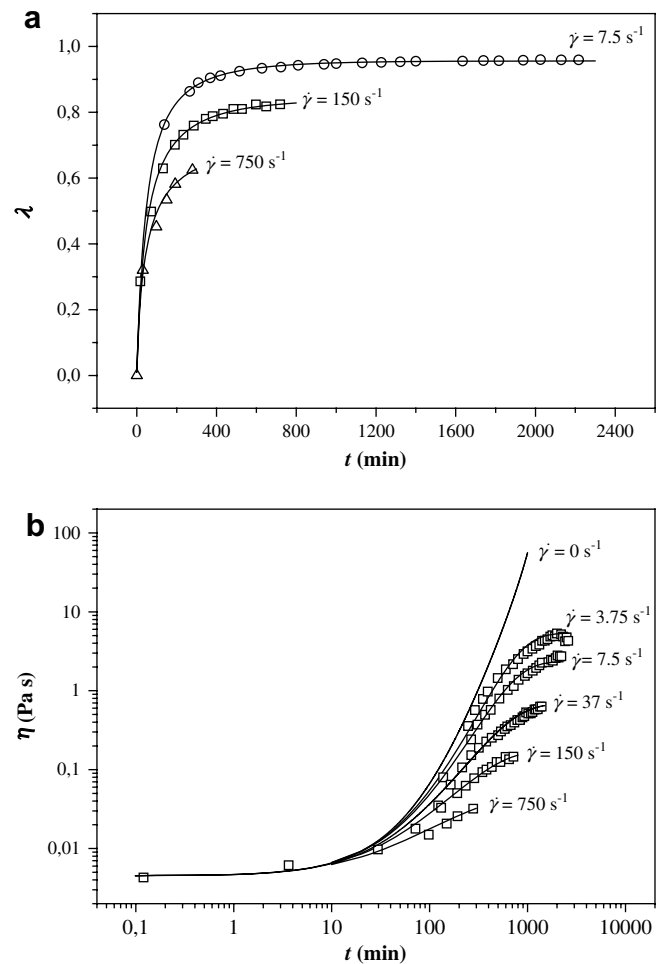
Another validation of the rheokinetic model framework was carried out by using experimental data of Sample IV concerning test A. The model fitting of experimental structural parameter and the prediction of apparent viscosity function are illustrated in Fig. 3a and b, respectively, where the characteristic functions and constants are reported in the figure caption. Once more, one observes a good performance of the rheokinetic model in a similar fashion as described in Figs. 1 and 2; in this case, the experimental information also covers higher values of maturation times making again more relevant the appropriate model response.



**Fig. 2.** (a) Normalized structural parameter  $\lambda$  and (b) apparent viscosity function  $\eta$  as a function of maturation time  $t$  for different shear rates following test A and protocol E-2. Symbols are experimental data of Sample III. Full lines are numerical predictions of the rheokinetic model, where parameters and functions are  $k = 1.2 \text{ s}^{-1}$ ,  $c = 1.1$ ,  $X = \dot{\gamma}^{1.17} / (1.078 \times 10^4 + 1.422 \times 10^3 \dot{\gamma} \ln \dot{\gamma})$  and  $q = 1.028 + 0.765 \dot{\gamma}^{0.22}$ .

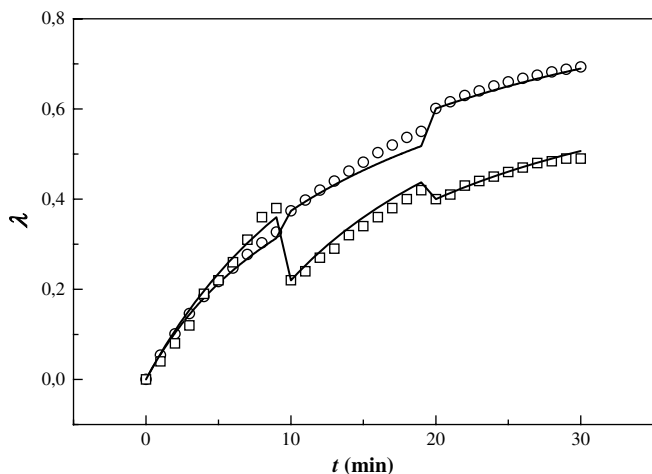
It is interesting to point out that the rheokinetic model proposed here also provides the gelling curve of the apparent viscosity function at the asymptotic zero shear rate, as illustrated in Figs. 1b, 2b and 3b, for  $\dot{\gamma} \rightarrow 0$ .

From Figs. 1 to 3, it is clear that despite the accepted performance of the model predictions for relatively high shear rates, functions  $X(\dot{\gamma})$  and  $q(\dot{\gamma})$  are rather undesirably complex for Samples III and IV (similar results were reported by Dullaert & Mewis, 2006, in a quite equivalent framework of modeling thixotropic responses for a fumed silica dispersion). Certainly these results indicate the strong non-linear response one should expect for thixotropic fluids expressed mainly through indirect structural kinetic models where, for instance, the mechanical breakdown function and the kinetic order of the build up process are considered to depend on shear rate. Through our numerical calculations we also found that although the functions  $X(\dot{\gamma})$  and  $q(\dot{\gamma})$  and constants  $k$  and  $c$  are the same for a given gelatin solution when one compares experimental data from other tests with the model numerical predictions (a constraint to be satisfied and already mentioned above), these functions and constants are not necessarily unique, as one should expect in general from fitting processes. Thus other set of functions, obtained from a typical software, are able to perform an appropriate prediction of experimental data. In this sense one chooses the set giving the best correlation coefficient  $r^2$  that is closer to unity. Typical values were  $r^2 > 0.99$  for the three gelatins studied here through test A.



**Fig. 3.** (a) Normalized structural parameter  $\lambda$  and (b) apparent viscosity function  $\eta$  as a function of maturation time  $t$  for different shear rates following test A and protocol E-2. Symbols are experimental data of Sample IV. Full lines are numerical predictions of the rheokinetic model, where parameters and functions are  $k = 2 \times 10^{-2} \text{ s}^{-1}$ ,  $c = 10^{-3}$ ,  $X = \dot{\gamma}^{0.5} / (7.591 \times 10^2 \dot{\gamma}^{0.5} + 4.010 \times 10^4)$  and  $q = 1.552 + 0.088 \dot{\gamma}^{0.5}$ .

In particular, Sample I of this work has the purpose to study other shear rate histories, which were not available for the other two samples reported in the literature. In fact, a more drastic test for the prediction capability of the rheokinetic model through Eq. (2) is depicted in Fig. 4, for the gelatin solution prepared in our laboratory, where test B is considered. This figure shows that the rheokinetic model proposed here fits well experimental data of the structural parameter for a sequence of three increasing and decreasing steps of shear rates (see protocol E-3 above). Nevertheless, after each sudden shear rate change, it is necessary to re-initialize the structural parameter  $\lambda$  to follow the correct stress level of the maturation evolution. This last result has two relevant conclusions. One of them indicates that for our gelatin solution (Sample I) reversibility is not satisfied because it was found that the re-initialization of  $\lambda$  cannot be imposed from the family of curves at different shear rates used to define the parameters and functions of the rheokinetic model with test A. For a more dilute gelatin solutions of around 3% (Sample IV) Huang and Sorensen (1996) showed that the reversibility condition is approximately valid for lower values of shear rate jumps. The other conclusion is that, the structural kinetic equation (Eq. (2)) can handle appropriately continuous mechanical histories only. Thus the model cannot predict the structural parameter around discontinuous changes of shear rates once the microstructure has been formed in some degree, what places further questions about the reversibility



**Fig. 4.** Normalized structural parameter  $\lambda$  as a function of maturation time  $t$  for three increasing and decreasing steps of shear rates, following test B and protocol E-3. Symbols are experimental data of Sample I. Shear rate histories are: ( $\square$ )  $\dot{\gamma} = 106 - 209 - 419 \text{ s}^{-1}$  and ( $\circ$ )  $\dot{\gamma} = 418 - 209 - 106 \text{ s}^{-1}$ . Full lines are numerical predictions of the rheokinetic model, where parameters and functions are the same as in Fig. 1.

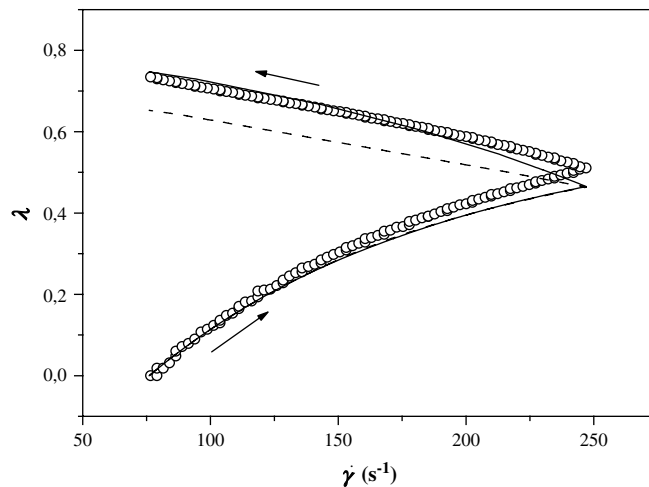
condition of these samples (see also below). It should be observed that, at the initial condition, the fluid viscosity is that of the non-matured solution, which is a quite Newtonian fluid, validating thus the use of test A to characterize the model; thus shear rate jumps are allowed at  $t = 0$  only.

A crucial test for the rheokinetic model is the thixotropic loop where a reversion of the mechanical history is introduced. To describe this important aspect, Fig. 5 shows numerical predictions of the rheokinetic model for a given thixotropic loop with a mechanical history indicated in protocol E-4. Parameters and functions used are the same as those allowing the fitting of experimental data of Fig. 1 (a constraint to be satisfied and already mentioned above). Through numerical results we found that for the decaying branch of shear rate, the shear stress response was consistent with the build up process only at the fixed value  $q(0)$ , indicating that the breakdown function was not relevant when  $d\dot{\gamma}/dt < 0$ . In this figure, the difference in numerical predictions is shown with a dashed line, which must be compared with the upper full line. In fact from these results we found that the structural kinetic equation (Eq. (2)) should be modified as follows:  $\dot{\lambda} = g(t, \dot{\gamma}^*(t))$ , where  $\dot{\gamma}^* = \dot{\gamma}(t)$  for  $d\dot{\gamma}/dt \geq 0$  and  $\dot{\gamma}^* = 0$  for  $d\dot{\gamma}/dt < 0$ . Here the effective shear rate  $\dot{\gamma}^*(t)$  is evaluated appropriately within the numerical algorithm through the rheometric shear rate history  $\dot{\gamma}(t)$  (see also Mujumdar et al., 2002, for a similar proposal concerning elastic deformations of thixotropic fluids for shear stresses below the yield value).

The existence of a yield value may be analyzed from Eq. (2). Since the relation between the true rheometric function  $\eta$  and the structural parameter is assumed generic enough and independent from any macroscopic model representing the fluid behavior, it is possible to show that this equation may be expressed, under the “quenching” hypothesis of the structural parameter, in terms for instance of the Bingham fluid, as follows,

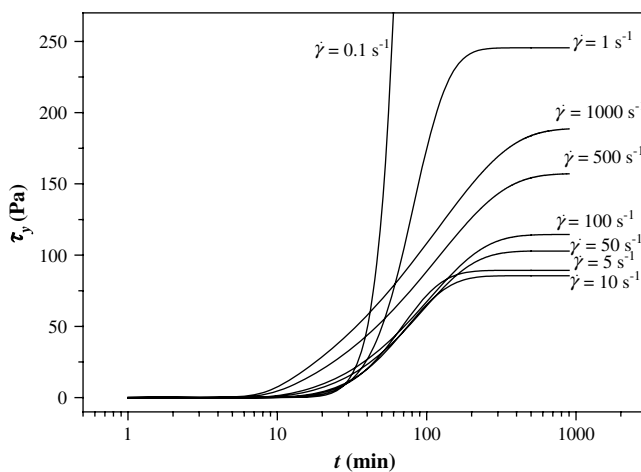
$$\eta(\lambda(t, \dot{\gamma}), \eta_s) = \tau_y(\lambda(\dot{\gamma}, t))/\dot{\gamma} + \eta_s = \eta_s / (1 - \lambda(\dot{\gamma}, t))^2 \quad (9)$$

Thus Eq. (9) allows one to express parameter  $\tau_y = \eta_s \{1 / (1 - \lambda(\dot{\gamma}, t))^2 - 1\} \dot{\gamma}$  as a function of  $\lambda(\dot{\gamma}, t)$ . Fig. 6 shows that the yield stress of maturing gelatin solutions increases with maturation time when the maturation process is carried out at constant shear rate. Even more interesting is the evolution of the yield stress with shear rate for a fixed value of the maturation time.



**Fig. 5.** Normalized structural parameter  $\lambda$  as a function of maturation time  $t$  for the thixotropic loop  $\dot{\gamma} = 76 - 247 - 76 \text{ s}^{-1}$  following test C and protocol E-4. Symbols are experimental data of Sample I. Full lines are numerical predictions of the rheokinetic model, where parameters and functions are the same as in Fig. 1 and the function  $\dot{\gamma}^* = \dot{\gamma}(t)$  is considered as described in the text. Dashed line uses  $\dot{\gamma}(t)$  directly.

Thus increasing the shear rate at any fixed time, parameter  $\tau_y$  increases as a consequence of the effective packing of smaller clusters formed with a rather similar structure volume fraction (see Section 4.2 below). In addition, for very small shear rates, Fig. 6 shows that a network is being formed with a sharp increment of the yield stress, which is a consequence of approaching the percolation point. Thus for shear rate values lower than  $50 \text{ s}^{-1}$ , other phenomena may be found like “stick-slip” flow or “fracture” reported and discussed clearly by De Carvalho and Djabourov (1997), and also found in our experiments. It is then clear that for low shear rates between the cluster suspension and the physically crosslinked network, further research is required with great challenges from the experimental point of view. Also, as long as  $\dot{\gamma}$  decreases from around  $50 \text{ s}^{-1}$ , thus for low shear rates below a critical value, the yield stress  $\tau_y$  may introduce a solid like zone within the flow domain, which is not homogenous (Møller et al., 2006). This phenomenon may be either associated to wall slip or eventually shear localization (see also Mewis, 1996 for a clear description of measurement problems involving concentrated suspensions). Our experiments for Sample I reveal that a critical



**Fig. 6.** Numerical predictions of yield stress  $\tau_y$  as a function of maturation time  $t$  for different shear rates as predicted by the rheokinetic model under the quenching assumption (Eq. (9)) for the gelatin solution (Sample III) characterized in Fig. 2.

shear rate is reached at around  $50 \text{ s}^{-1}$  in coincidence with the results available for Sample III. This phenomenon was not found for Sample IV despite a similar shear rate range was applied, perhaps due to the use of lower gelatin concentration (around 3%) and average molecular weight.

#### 4.2. Estimations of cluster radius evolutions from experimental data

Eq. (1) is related to theoretical results of suspension rheology. In this framework estimations of average cluster sizes may be carried out by extending a previous analysis (Olivares, Peirotti, & Deiber, 2006) concerning the aggregation of dilute maturing gelatin solutions to more concentrated ones, by eliminating those equations valid for the dilute regime only. Thus, it is well known that when the ratio  $\phi_{\text{eff}}/\phi_c$  between the effective volume fraction  $\phi_{\text{eff}}$  of clusters accounting the occluded solvent and the critical locking volume fraction  $\phi_c \approx 0.63$  (for instance random close packing; Mewis, 1996) tends to unity, an infinite value of the apparent viscosity function is obtained as long as the shear rate is asymptotically zero (Berli, Deiber, & Añón, 1999a, 1999b; Berli, Deiber, & Quemada, 2005; Quemada & Berli, 2002). This result is expressed as  $\eta/\eta_w = 1/(1 - \phi_{\text{eff}}/\phi_c)^2$ , where  $\eta_w$  is the aqueous solvent viscosity and  $\phi_{\text{eff}} = \phi N^{(3-f)/f}$  with a cluster fractal  $f$  and an initial volume fraction of the discrete phase  $\phi$  (Lin et al., 1989; Quemada, 1989). Also,  $N = n_o/n_T$  is the number average of kinematical units per cluster at a given maturation time and shear rate, where  $n_T$  is the total number of clusters at the same conditions, and  $n_o = C_m N_A / M_n$  is the density number of initial chains evaluated with the protein mass concentration  $C_m$  and the Avogadro number  $N_A$  (Russel, Saville, & Schowalter, 1989). For the three gelatin solutions studied here, the rheokinetic model predictions of the apparent viscosity function indicate that  $N$  starts from one (initial kinematical units are considered equivalent spheres of each gelatin chain) and tends to be a constant value at high maturation times where equilibrated clusters are obtained (see Fig. 7). Thus for high times,  $N$  becomes non-linearly saturated toward a constant value indicating that the structure breakdown due to shear rate becomes important, and that the equilibrium  $\lambda \rightarrow \lambda_e$  is achieved, where the average cluster size becomes constant on time. This description is coincident with previous results reported by De Carvalho and Djabourov (1997). It is also clear that with the above relationships the average radius of clusters at any time and shear rate may be estimated from  $R(t) = N(t)^{1/f} a$  (Russel et al., 1989) where  $a$  is the initial average radius of the spherical solvated particles. Therefore, the average

radius evolutions of the two bone gelatin solutions (Samples III and IV) are shown in Fig. 8. Important is to visualize in this figure that the cluster equilibrium radius decreases as shear rate increases. It is also found that the gelatin solution with lower protein concentration and molecular weight (Sample IV) yields the higher equilibrium cluster radius, when the two bone gelatins are compared. Further, the fractal value  $f \approx 2.86$  estimated here allowed us to get equilibrium cluster radii of the same order as those reported by De Carvalho and Djabourov (1997). These authors used the critical Peclet number ( $\eta_s \dot{\gamma} R^3 / k_B T \approx 1$ ) at which shear rate starts to be relevant in the breakdown process of microstructure. Certainly, this fractal value indicates that clusters formed may be rather compact. This conclusion is expected having into account that helix junction zones and some annealing involving random chains occur along time for the aggregation of gelatin chains.

#### 4.3. Model predictions for different gelatin concentrations

As a final step of this work, the rheokinetic model was tested for different concentrations of gelatin solutions. For this purpose Sample II described in Section 2.1 was used at the following solution concentrations: 4, 7, 8.7, 10, 11 and 12% w/w. The functions and parameters of the rheokinetic model were appropriately evaluated by fitting rheometric data obtained in shear flow (test A) with a correlation coefficient  $r^2 > 0.993$  (see also Fig. 9). In regard to these results several aspects deserve to be presented here. Thus it is found that as gelatin concentration increases the power  $c$  becomes smaller indicating that the gelling process increases substantially from early times at the high concentration range (see also in Section 3.2 above, the description concerning the effect if this parameter on the model response). Further, the relevance of this parameter at low concentrations is effectively observed because the breakdown of structure due to shear competes remarkably with the build up process as illustrated in Fig. 9 for  $\dot{\gamma} = 153.6 \text{ s}^{-1}$ . Interesting is the case for the 4% w/w solution of this gelatin sample, where the structural parameter  $\lambda$  calculated from experimental data remains constant during test A for  $\dot{\gamma} > 76 \text{ s}^{-1}$  indicating that the breakdown process exceeds the rate of network formation. Thus gelatin maturation may be inhibited due to shear forces at a given value of gelatin concentration, which depends of course on the specific properties of the gelatin type selected. These situations are usually manifested by unstable measurement of the shear rate viscosity when low concentration and bloom values are used in the formulation of gelatin solutions.

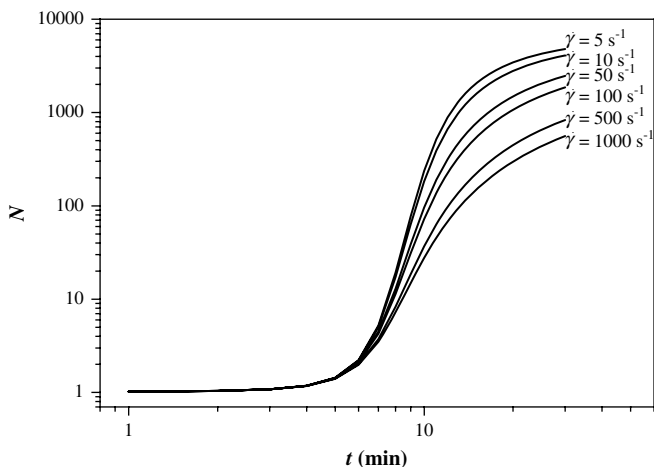


Fig. 7. Numerical predictions of average number of kinematical units per cluster  $N$  as a function of maturation time  $t$  at different shear rates for Sample III characterized in Fig. 2.

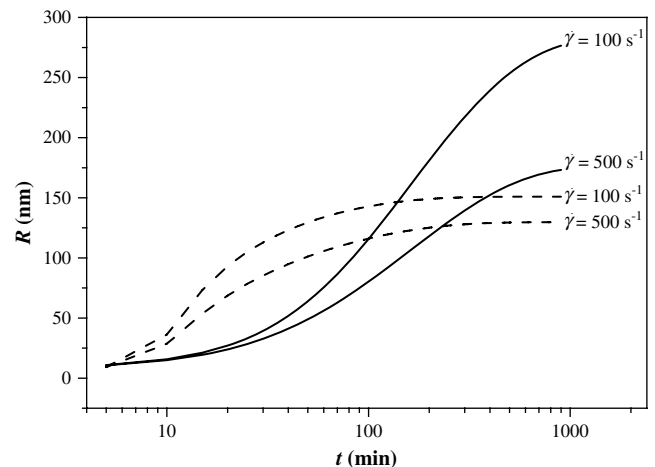


Fig. 8. Numerical predictions of average cluster radius  $R(t)$  as a function of maturation time  $t$  at two different shear rates. Dashed and full lines refer to Samples III and IV, characterized in Figs. 2 and 3, respectively.



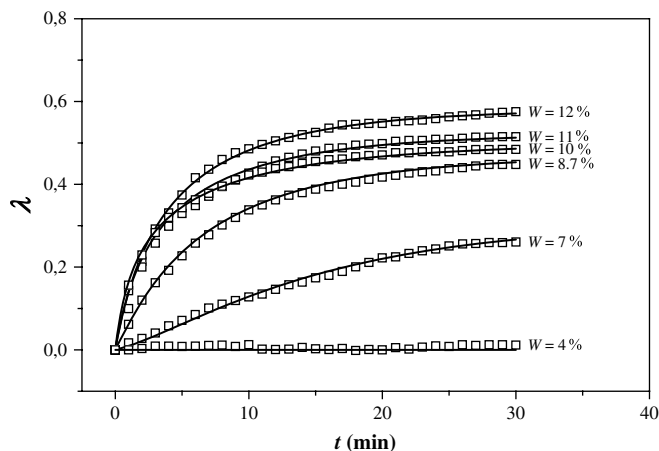


Fig. 9. Normalized structural parameter  $\lambda$  as a function of maturation time  $t$  for different concentrations of Sample II at  $\dot{\gamma} = 153.6 \text{ s}^{-1}$  and  $26^\circ\text{C}$ . Symbols are experimental data from test A. Full lines are numerical predictions of the rheokinetic model.

Another relevant aspect of the gelatin under study here is that the kinetic constant  $k$  associated with the rate of gelling or build up process (Eq. (2)) presents a rather simple correlation with protein concentration  $W$  (% w/w), which is expressed as  $k \approx W^2 \times 10^{-3} / (1 - 0.004W^2)$  with  $r^2 > 0.9998$ . Thus, this relation shows that the formation of structure at relatively low concentrations, within the gelling regime, presents the expected second order response.

## 5. Conclusions

Numerical results of the rheokinetic model proposed fit well experimental rheometric data obtained in shear flow for the maturing evolution of different gelatin solutions. Different steps of shear rates are used for a consistent evaluation of parameters and functions included in the structural kinetic equation. A shear rate function involving reversion of the rate of deformation history at a defined time describes the complexity of thixotropic phenomena associated with maturing gelatin solutions. Predictions in general indicate the progresses and limitations of modeling the phenomenon of rheokinetic gelling, requiring more accurate rheological constitutive models.

From our studies it is possible to conclude that: (1) The rheokinetic evolution of the structural parameter may be carried out within the context of thixotropic theories. (2) The structural parameter may be evaluated directly from the apparent viscosity measurements as long as the shear rate histories are designed so that the instantaneous values of shear rates are above the critical one to avoid shear instabilities due to yield stress, a phenomenon appearing in most thixotropic fluids. (3) Within the experimental and allowed fitting errors, it is not possible in general to propose unique parameters and functions for the structural kinetic model. (4) In particular we found that for maturing aqueous gelatin solutions, the general framework described by Eqs. (1) and (2) and the asymptotic analytic solutions are appropriate when the breakdown rate process and the order of the build up rate process are functions of shear rate. (5) The maturing of gelatin solutions is quite sensitive to the sign of the rate of variation of shear rate. Thus reversing shear rates from high to lower values, the breakdown process seems to be ineffective and the microstructure evolution is controlled mainly by the build up process only. On the contrary for increasing shear rate history both build up and breakdown processes are important,

mainly at high times of maturation where an equilibrium structural parameter is found.

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